

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2000-279814

(P2000-279814A)

(43) 公開日 平成12年10月10日 (2000. 10. 10)

(51) Int. CL ⁷	識別記号	F I	7-73-1 [*] (参考)
B 0 1 J 23/63		B 0 1 J 23/58	3 0 1 A 4 D 0 4 8
B 0 1 D 53/86	Z A B	B 0 1 D 53/36	Z A B 4 G 0 6 9
53/94			1 0 2 B
			1 0 2 H

審査請求 未請求 請求項の数 7 O L (全 8 頁)

(21) 出願番号 特願平11-92105

(22) 出願日 平成11年3月31日 (1999. 3. 31)

(71) 出願人 00003997

日産自動車株式会社

神奈川県横浜市神奈川区宝町2番地

(72) 発明者 花木 保成

神奈川県横浜市神奈川区宝町2番地 日産

自動車株式会社内

(72) 発明者 菅 克雄

神奈川県横浜市神奈川区宝町2番地 日産

自動車株式会社内

(74) 代理人 100059258

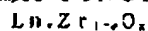
弁理士 杉村 曉秀 (外8名)

最終頁に続く

(54) 【発明の名称】 排気ガス浄化用触媒及びその使用方法

(57) 【要約】

【課題】 従来の触媒では十分な活性を示さなかったリーン雰囲気下におけるNO_x浄化性能を向上させることができ、かつ三元触媒としての機能を十分に発現することができる排気ガス浄化用触媒及びそのNO_x浄化作用*



(式中、0.4 < α < 0.9、xは各原子の価数を満足する酸量、

L_n = La, Pr & Ndから成る群より選ばれた少なくとも一種

を示す)

で表される複合酸化物とを含有する。

*が特に有効に発現できる使用方法を提供する。

【解決手段】 排気ガス浄化用触媒は、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも一種の貴金属と、次の一般式

【数1】

(2)

特開2000-279814

1

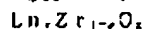
2

【特許請求の範囲】

* 群より選ばれた少なくとも一種の貴金属と、次の一般式

【請求項1】 白金、パラジウム及びロジウムから成る*

【数1】



(式中、0.4 < x < 0.9、xは各原子の価数を満足する酸素量、

Ln=L a、Pr及びNdから成る群より選ばれた少なくとも一種

を示す)

で表されるペロブスカイト型複合酸化物とを含有することを特徴とする排気ガス浄化用触媒。

【請求項2】 複合酸化物は、排気ガス浄化用触媒1Lあたり30～100g含有されることを特徴とする請求項1記載の排気ガス浄化用触媒。

【請求項3】 更に、アルミナを、排気ガス上記用触媒1Lあたり100～300g含有することを特徴とする請求項1又は2記載の排気ガス浄化用触媒。

【請求項4】 無機担体上に少なくとも2層を設けた構造から成り、上記複合酸化物を含む層を下層に、上記複合酸化物を含まない層を上層に設けて成ることを特徴とする請求項1～3いずれかの項記載の排気ガス浄化用触媒。

【請求項5】 触媒層を構成する材料の平均粒径が4μm以下であることを特徴とする請求項1～4いずれかの項記載の排気ガス浄化用触媒。

【請求項6】 請求項1～5いずれかの項記載の排気ガス浄化用触媒を、空燃比が10～50の範囲を繰り返すリーンバーンエンジン車に使用することを特徴とする、排気ガス浄化用触媒の使用法。

【請求項7】 請求項1～5いずれかの項記載の排気ガス浄化用触媒を、空燃比が10～14.8と、15～50の範囲とを繰り返すリーンバーンエンジン車に使用することを特徴とする排気ガス浄化用触媒の使用法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、自動車、ボイラー等の内燃機関から排出される排気ガス中の炭化水素（HC）、一酸化炭素（CO）および窒素酸化物（NOx）を浄化する排気ガス浄化用触媒及びその使用方法に関し、特に酸素過剰雰囲気下でのNOxの浄化性能に優れた排気ガス浄化用触媒及びその使用方法に関する。

【0002】

【従来の技術】従来より、自動車の排気ガス浄化用触媒としては、CO及びHCの酸化とNOxの還元とを同時に行って排気ガスを浄化する三元触媒が用いられている。三元触媒としては、例えばコージュライトなどの耐火性担体にγ-アルミナなどから担持層を形成し、その担持層にPt、Pd、Rhなどの貴金属触媒を担持させたものが広く知られている。

【0003】このような排気ガス浄化用触媒の浄化性能は、エンジンの空燃比（A/F）によって大きく異なる。すなわち、空燃比の大きい、つまり燃料濃度が希薄

なリーン側では、排気ガス中の酸素量が多くなり、COやHCを浄化する酸化反応が活発である反面、NOxを浄化する還元反応が不活性になる。逆に空燃比の小さい、つまり燃料濃度が濃いリッチ側では、排気ガス中の酸素量が少なくなり、酸化反応は不活性となるが還元反応は活発になる。

【0004】一方、自動車の走行において、市街地走行の場合には発進・停止が頻繁に行われ、空燃比は理論値近傍からオーバーリーン状態までの範囲内で頻繁に変化する。このような走行における低燃費化の要請に応えるには、なるべく酸素過剰の混合気を供給するリーン側での運転が必要となる。したがってリーン側においてもNOxを十分に浄化できる触媒の開発が望まれている。

【0005】従来より、リーン雰囲気下におけるNOx浄化性能を向上させる触媒は種々提案されており、例えば特開平5-168860号公報には、ランタン等を白金（Pt）に担持させてランタンをNOx吸収材として用いる触媒が開示されている。これはリーン雰囲気下でNOxを吸収し、ストイキ状態あるいは燃料過剰（リッチ）雰囲気下でNOxを放出浄化するものである。

【0006】しかしながら、上記従来のNOx吸収触媒（例えばPt-ランタン触媒）は、その特性上、リーン雰囲気下で定常走行を行うとNOx吸収量が飽和に達してやがて吸収作用が消失するという問題があり、NOx浄化性能が不足し、耐久後の性能も十分でなく、幅広い運転条件下でNOxを浄化することができない。

【0007】

【発明が解決しようとする課題】従って、請求項1～5記載の発明の目的は、従来の触媒では十分な活性を示さなかったリーン雰囲気下におけるNOx浄化性能を向上させることができ、かつ三元触媒としての機能を十分に発揮することができる排気ガス浄化用触媒を提供するにある。

【0008】また、請求項6又は7記載の発明の目的は、本発明の排気ガス浄化用触媒のそのNOx浄化作用が特に有効に発揮できる排気ガス浄化用触媒の使用法を提供するにある。

【0009】

【課題を解決するための手段】請求項1記載の排気ガス浄化用触媒は、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも一種の貴金属と、次の一般式

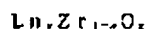
【数2】

(3)

特開2000-279814

3

4

(式中、 $0.4 < \alpha < 0.9$ 、 x は各原子の価数を満足する酸素量、 $L_n = La, Pr$ 及び Nd から成る群より選ばれた少なくとも一種

を示す)

で表される複合酸化物とを含有することを特徴とする。

【0010】請求項2記載の排気ガス浄化用触媒は、請求項1記載の排気ガス浄化用触媒において、複合酸化物が、排気ガス浄化用触媒1Lあたり30～100g含有されることを特徴とする。

【0011】請求項3記載の排気ガス浄化用触媒は、請求項1又は2記載の排気ガス浄化用触媒において、更に、アルミナを、排気ガス上記用触媒1Lあたり100～300g含有することを特徴とする。

【0012】請求項4記載の排気ガス浄化用触媒は、請求項1～3いずれかの項記載の排気ガス浄化用触媒において、無機担体上に少なくとも2層を設けた構造から成り、上記複合酸化物を含む層を下層に、上記複合酸化物を含まない層を上層に設けて成ることを特徴とする。

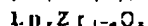
【0013】請求項5記載の排気ガス浄化用触媒は、請求項1～4いずれかの項記載の排気ガス浄化用触媒において、触媒層を構成する材料の平均粒径が4 μm 以下であることを特徴とする。

【0014】また、上記本発明の排気ガス浄化用触媒の有効な NO_x 吸収、放出サイクルを発生させるために、請求項6記載の排気ガス浄化用触媒の使用方法是、本発明の排気ガス浄化用触媒を、空燃比が10～50の範囲とを繰り返すリーンバーンエンジン車に使用することを特徴とする。

【0015】請求項7記載の排気ガス浄化用触媒は、請求項1～5いずれかの項記載の排気ガス浄化用触媒を、空燃比が10～14.8と、15～50の範囲とを繰り返すリーンバーンエンジン車に使用することを特徴とする。

【0016】

【発明の実施の形態】本発明の排気ガス浄化用触媒中の*

(式中、 $0.4 < \alpha < 0.9$ 、 x は各原子の価数を満足する酸素量、 $L_n = La, Pr$ 及び Nd から成る群より選ばれた少なくとも一種

を示す)

で表される。

【0020】本発明の排気ガス浄化用触媒に用いられる複合酸化物には、希土類金属と、遷移金属とが含まれる。希土類金属としては、ランタン、プラセオジム及びネオジムが、また遷移金属としては、ジルコニウムが好適に使用できる。

【0021】このような複合酸化物は、希土類金属と、アルミナとの複合化が回避されることにより、耐久後で

* 貴金属には、白金、パラジウム及びロジウムから成る群より選ばれる少なくとも1種が用いられる。例えばPtとRh、PdとRh、Pdのみ等の種々の組み合わせが可能である。前記貴金属の含有量は、 NO_x 吸収能と三元触媒性能が十分に得られれば特に限定されないが、0.1gより少ないと十分な三元性能が得られず、10gより多く使用しても有意な特性向上はみられない点から、本発明の排気ガス浄化用触媒1Lあたり0.1～10gが好ましい。

【0017】本発明の触媒はストイキ時の三元触媒としての機能も必要であるため、上記貴金属は、少なくとも一部が無機担体の多孔質体に担持されることが好ましく、特にアルミナに担持されることが好ましい。ここで用いるアルミナは耐熱性の高いものが好ましく、なかでも比表面積が50～300 m^2/g の活性アルミナが好ましい。またアルミナの耐熱性を向上させるために、従来から三元触媒で適用されているように、セリウム、ランタン等の希土類化合物やジルコニウムなどの添加物をさらに加えてもよい。またその含有量は、排気ガス浄化用触媒1Lあたり100～300gとすることが、貴金属、特にPdのもの NO_x 吸収反応に必要な NO_x 酸化活性が最大限に発揮される点から好ましい。

【0018】更に本発明で用いる触媒は、ストイキ時の三元触媒としての機能も必要であるため、従来から三元触媒で用いられている添加物を更に加えても良く、例えば酸素ストレージ機能を有するセリアや、貴金属へのH₂C吸着脱着を緩和するバリウムや、Rhの耐熱性向上に寄与するジルコニア等である。

【0019】また本発明の排気ガス浄化用触媒中に含まれる複合酸化物は、次の一般式

【数3】

も NO_x の吸着が容易になり、リーン雰囲気において NO_x を吸収するという特性を利用することにより、 NO_x の浄化性能を向上させることが可能となっている。

【0022】 α の値は、0.9以上だと希土類金属の単独の酸化物と同等である。0.4以下だと、希土類元素のもつ NO_x 吸着能が低下し、十分な NO_x 浄化性能が得られないので、 $0.4 < \alpha < 0.9$ であることが好ましい。 x の値は各原子の価数を満足する酸素量であり、

(4)

特開2000-279814

5

およそ $0 < \delta < 4$ 程度である。

【0023】ランタン、プラセオジウム、ネオジウムから成る群より選ばれる少なくとも1種が、Zrとペロブスカイト型の複合酸化物を形成することにより、これらの希土類金属とアルミナの複合化が回避され、耐久後でもNO_x吸着が容易となる。複合酸化物が形成されていない場合、たとえば、La₂O₃とZrO₂とを混合したのでは、特に、耐久後においてNO_x吸着性能が大きく低下してしまう。

【0024】本発明で用いられる複合酸化物は、リーン雰囲気下でNO_xを吸収する性能を発現させるが、その吸収機構は、気相中のNO_xが貴金属上でNO₂に酸化され、それが複合酸化物上でさらにNO₃となり、複合酸化物上に吸収される。従ってリーン雰囲気下でNO_xを有効に吸収するための複合酸化物の組成は、NO₃塩を作りやすいという作用を有するLa、Pr及びNdから成る群より選ばれた少なくとも1種の元素を含有し、Zrと複合化していることが重要である。

【0025】該複合酸化物の各構成元素は、触媒に含まれるこれらの全てが複合化している場合に、その上記した作用は最大限に発揮されるが、少なくとも一部が複合体を形成しうる場合でも十分に上記作用を得ることができる。

【0026】該複合酸化物の各構成元素は、熱耐久後でも別々の酸化物として分解することなく複合酸化物として存在することができ、これは例えばX線回折測定により確認することができる。

【0027】該複合酸化物中の各構成元素には、その上記作用を妨げる量でなければ微量の不純物を含んでも構わず、例えばバリウム中に含まれるストロンチウムや、ランタン中に含まれるセリウム、ネオジウム、サマリウムやジルコニウム中に含まれるハフニウムやイオウ等である。

【0028】前記複合酸化物粉末は、その作用が得られる量が触媒中に含有されれば特に含有量は限定されないが、本発明の排気ガス浄化用触媒1あたり30～100g含有されることが、十分かつ有意義なNO_x吸着を得る点から好ましい。

【0029】本発明の排気ガス浄化用触媒は、前記貴金属と、複合酸化物とを共存させることにより、各々単独では得られないNO_x浄化作用を得ることが可能となっている。即ち、排気ガス雰囲気が一リーンとなった場合には、本発明の排気ガス浄化用触媒中の複合酸化物によるNO_x吸着作用により、高いNO_x浄化性能が得られる。該複合酸化物のNO_x吸着し、また排気ガス雰囲気が一リーンからストイキに変化すると該複合酸化物からNO_xが放出され、高いNO_x浄化性能が得られる。該複合酸化物を構成する各成分の単独物を単に混合しただけでは得られない優れたNO_x浄化性能を得るものである。

5

【0030】本発明の他の排気ガス浄化用触媒は、耐火性無機担体上に少なくとも2層を設けた構造から成り、上記複合酸化物を含む層を下層に、上記複合酸化物を含まない層を上層に設けて成る。

【0031】このように多層構造化し、複合酸化物を内層に含有せしめることで、ストイキ～リッチ時に放出されるNO_xを効率よく浄化できることとなり、また三元触媒機能のうちのHC浄化機能の低下を抑制することができる。即ち、放出NO_xを有効に浄化するには、複合酸化物を含まない上層に配置することが良く、このような構造とすることにより複合酸化物を含む内層でNO_xを吸収し、複合酸化物を含まない上層で放出NO_xを浄化することとなり、更に十分な三元触媒機能を得ることができる。

【0032】本発明の触媒層を構成する材料の平均粒径（メジアン径）は4μm以下であることが好ましい。粒径をこのような範囲とすることで、リーン時のNO_x吸着能力を向上させることができる。

【0033】即ち、排気ガス浄化用触媒は、ガス流れ速度を遅くすると優れたNO_x吸着作用を発揮でき、このような効果は、上記範囲の平均粒径とすることで達成され、その結果高いNO_x吸着活性を得ることができるのである。

【0034】更に、かかる平均粒径とすることによって、好ましくは本発明の排気ガス触媒中に好適に担持される貴金属を高分散化し、NO_x吸着作用を高めることもできる。

【0035】特に、前記効果を更に向上させるためには、平均粒径は2～4μmであることが好ましい。本明細書における平均粒径は、レーザー回折型粒度分布計により測定されたものである。

【0036】本発明に用いる複合酸化物は、複合酸化物の各構成元素の硝酸塩、酢酸塩、炭酸塩、クエン酸、塩酸塩等を、所望する複合酸化物の組成比に混合し、仮焼成した後粉砕して、熱処理焼成する固相反応や、複合酸化物の各構成元素の硝酸塩、酢酸塩、炭酸塩、塩酸塩、クエン酸塩等を、所望する複合酸化物の組成比に混合し、水に溶解した後、必要に応じてNH₃、OH⁻やNH₄⁺、CO₂等のアルカリ溶液を滴下して沈殿物を生成し、ろ過した後沈殿物を乾燥させて焼成する共沈法により調製することができるが、これらの方法に限定されるものではなく、前記以外の方法でも複合酸化物が形成されるものであればよい。

【0037】かかる方法により、複合酸化物を構成する各成分の少なくとも一部を複合化することができる。

【0038】本発明で用いる複合酸化物の触媒調製用原料には、前記したように、その上記作用を妨げる量でなければ微量の不純物を含んでも構わず、例えば希土類金属中に含まれるセリウム、ネオジウム、サマリウムや、ジルコニウム中に含まれるハフニウムやイオウ等である。

(5)

特開2000-279814

7

8

【0039】本発明に用いる貴金属の貴金属原料化合物としては、無機酸塩、炭酸塩、アンモニウム塩、有機酸塩、ハロゲン化物、酸化物、ナトリウム塩、アンミン錯化合物等を組み合わせて使用することができるが、特に水溶性の塩を使用することが触媒性能を向上させる観点から好ましい。貴金属の多孔質体への担持法としては特殊な方法に限定されず、成分の著しい偏在を伴わない限り、公知の蒸発乾燥法、沈殿法、含浸法、イオン交換法等の種々の方法を用いることができる。特にアルミナへの担持には、分散性を高める点から含浸法が好ましい。

【0040】イオン交換法、含浸法による場合、金属原料は溶液で用いることが多いため、その溶液に酸あるいは塩基を添加して、pHを調節することもできる。pHを調節することにより、更に、高分散担持できる可能性もある。

【0041】本発明の触媒は、一体構造型担体に担持して用いるのが好ましく、複合酸化物、貴金属担持無機担体を粉碎してスラリーとし、触媒担体にコートして、400～900℃の温度で焼成することにより、本発明の排気ガス浄化用触媒を得ることができる。

【0042】複合酸化物、貴金属担持無機担体を粉碎するにあたっての粉碎方法は特に限定されず、好ましくはこれらを含む水性スラリーを湿式粉碎して、平均粒径が4μm以下となるように調整する方法を用いることができる。

【0043】粉碎に使用することのできる装置は特に限定されず、市販のボール式振動ミルを用いることができ、ボール径、粉碎時間、振幅、振動周波数を調整して所望の粒径を得る。

【0044】触媒担体としては、公知の触媒担体の中から適宜選択して使用することができ、例えば耐火性材料からなるモノリス構造を有するハニカム担体やメタル担体等が挙げられる。

【0045】この触媒担体の形状は、特に制限されないが、通常はハニカム形状で使用する事が好ましく、このハニカム材料としては、一般に例えばセラミックス等のコージュライト質のものが多く用いられるが、フェライト系ステンレス等の金属材料からなるハニカムを用いることも可能であり、更に触媒粉末そのものをハニカム形状に成形しても良い。触媒の形状をハニカム状とすることにより、触媒と排気ガスの触媒面積が大きくなり、圧力損失も抑えられるため自動車用等として用いる場合に極めて有利である。

【0046】上記本発明の排気ガス浄化用触媒は、その使用条件を特に限定されないが、好ましくは空燃比が10～50、更に好ましくは空燃比が10～14.8と15～50の範囲とを繰り返すリーンバーンエンジン車に使用することができる。このような使用方法とすることにより、NOx吸収・放出のサイクルが極めて有効に成立し、特に効率の良いNOx浄化が可能となる。即ち、

空燃比が10～50の範囲内の空燃比の大きな領域（リーン領域）でNOxを吸収し、空燃比の小さな領域（リッチおよび/またはストイキ）でNOxを浄化することにより、高いNOx浄化性能を得ることができるのであり、さらに好適な範囲は、空燃比の小さな領域が10から14.8、空燃比の大きな領域が15～50である。

【0047】

【実施例】以下、本発明を次の実施例及び比較例により説明する。

10 実施例1

硝酸Pd水溶液を活性アルミナ粉末に含浸し、乾燥後、空气中400℃で1時間焼成して、Pd担持アルミナ粉末（粉末1）を得た。この粉末1のPd濃度は2.8重量%であった。ジエトロジアミンPt水溶液を活性アルミナ粉末に含浸し、乾燥後、空气中400℃で1時間焼成して、Pt担持アルミナ粉末（粉末2）を得た。この粉末2のPd濃度は2.8重量%であった。硝酸Rh水溶液を活性アルミナ粉末に含浸し、乾燥後、空气中400℃で1時間焼成して、Rh担持アルミナ粉末（粉末3）を得た。この粉末3のRh濃度は0.7重量%であった。

【0048】炭酸ランタンと硝酸ジルコニウムの混合物にクエン酸を加え、乾燥後700℃で焼成し、La-Zr複合酸化物粉末（粉末4）を得た。この粉末4は金属原子比でランタン/ジルコニウム=5/5であった。

【0049】上記粉末1を180g、上記粉末2を90g、上記粉末4を180g、水360gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時のスラリーの平均粒径は2.8μmであった。このスラリー液をコーディライト質モノリス担体（1.3L、400セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて130℃で乾燥した後、400℃で1時間焼成し、コート層重量125g/L-担体の触媒（A）を得た。

【0050】上記粉末1を90g、上記粉末2を90g、粉末3を180g、水360gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8μmであった。このスラリー液を上記触媒（A）に付着させて、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、総コート層重量250g/L-担体の排気ガス浄化用触媒を得た。

【0051】実施例2

粉末4のLaをNdに代えた以外は、実施例1と同様の方法で排気ガス浄化用触媒を得た。

【0052】実施例3

粉末4のLaをPrに代えた以外は、実施例1と同様の方法で排気ガス浄化用触媒を得た。

【0053】実施例4

実施例1で得られた粉末1を180g、粉末2を180

(5)

特開2000-279814

9

g、粉末3を180g、粉末4を180g、水720gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8 μ mであった。このスラリー液をコーディライト質モノリス担体(1.3L、400セル)に付着させて、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、コート層重量250g/L-担体の排気ガス浄化用触媒を得た。

【0054】比較例1

粉末4を除き、代わりにLaを6mol%添加した活性アルミナ粉末を用いた以外は、実施例1と同様の方法で排気ガス浄化用触媒を得た。

【0055】比較例2

スラリーの平均粒径を8 μ mに調整した以外は、実施例1と同様の方法で排気ガス浄化用触媒を得た。

【0056】比較例3

実施例1で得られた粉末1を90g、粉末2を90g、粉末3を180g、水360gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8 μ mであった。このスラリー液をコーディライト質モノリス担体(1.3L、400セル)に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、コート層重量125g/L-担体の触媒(B)を得た。

【0057】実施例1で得られた粉末1を90g、粉末2を90g、粉末4を180g、水360gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8 μ mであった。このスラリー液を触媒(B)に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、総コート層重量250g/L-担体の排気ガス浄化用触媒を得た。

【0058】比較例4

実施例1で得られた粉末1を90g、粉末2を90g、粉末4を60g、活性アルミナを120g、水360gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8 μ mであった。このスラリー液をコーディライト質モノリス担体(1.3L、400セル)に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、

10

400℃で1時間焼成し、コート層重量125g/L-担体の触媒(C)を得た。

【0059】実施例1で得られた粉末1を90g、粉末2を90g、粉末3を180g、水360gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8 μ mであった。このスラリー液を触媒(C)に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、総コート層重量250g/L-担体の排気ガス浄化用触媒を得た。

【0060】比較例5

実施例1で得られた粉末1を90g、粉末2を90g、粉末4を360g、水540gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8 μ mであった。このスラリー液をコーディライト質モノリス担体(1.3L、400セル)に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、コート層重量187.5g/L-担体の触媒(D)を得た。

【0061】実施例1で得られた粉末1を90g、粉末2を90g、粉末3を180g、水360gを磁性ボールミルに投入し、混合粉碎してスラリー液を得た。この時の、スラリーの平均粒径は2.8 μ mであった。このスラリー液を触媒(D)に付着して、空気流にてセル内の余剰のスラリーを取り除き130℃で乾燥した後、400℃で1時間焼成し、総コート層重量312.5g/L-担体の排気ガス浄化用触媒を得た。

【0062】比較例6

実施例1において、粉末4のかわりにLa、O、45g ZrO₂、135gを用いた以外は、実施例1と同様の方法で、排気ガス浄化用触媒を得た。

【0063】比較例7

実施例1において、粉末4を、LaとZrの比がLa/Zr=1/9にした以外は同様の方法で、排気ガス浄化用触媒を得た。

【0064】前記実施例1～4及び比較例1～7で得られた排気ガス浄化用触媒の触媒組成を表1に示す。

【0065】

【表1】

(7)

特開2000-279814

11

12

組 成 表

	貴金属(g/L)			2-1 層構造	複合酸化物の位置	複合酸化物量(g)	スラリー粒 径	複合酸化物組成
	Pt	Pd	Rh					
実施例1	1.75	1.75	0.43	2層	下層	180	2.8 μ m	La _{0.5} Zr _{0.5} O _x
実施例2	1.75	1.75	0.43	2層	下層	180	2.8 μ m	Nd _{0.5} Zr _{0.5} O _x
実施例3	1.75	1.75	0.43	2層	下層	180	2.8 μ m	Pr _{0.5} Zr _{0.5} O _x
実施例4	1.75	1.75	0.43	1層	—	180	2.8 μ m	La _{0.5} Zr _{0.5} O _x
比較例1	1.75	1.75	0.43	2層	下層	180	2.8 μ m	La _{0.5} Zr _{0.5} O _x -Al ₂ O ₃
比較例2	1.75	1.75	0.43	2層	下層	180	8 μ m	La _{0.5} Zr _{0.5} O _x
比較例3	1.75	1.75	0.43	2層	上層	180	2.8 μ m	La _{0.5} Zr _{0.5} O _x
比較例4	1.75	1.75	0.43	2層	下層	60	2.8 μ m	La _{0.5} Zr _{0.5} O _x
比較例5	1.75	1.75	0.43	2層	下層	360	2.8 μ m	La _{0.5} Zr _{0.5} O _x
比較例6	1.75	1.75	0.43	2層	—	La ₂ O ₃ 45g ZrO ₂ 135g	2.8 μ m	La ₂ O ₃ +ZrO ₂
比較例7	1.75	1.75	0.43	2層	下層	180	2.8 μ m	La _{0.5} Zr _{0.5} O _x

【0066】試験例

前記実施例1～4及び比較例1～7で得られた排気ガス浄化用触媒について、以下の条件で初期及び耐久後の触媒活性評価を行った。活性評価には、自動車の排気ガスを模したモデルガスを用いる自動評価装置を用いた。

【0067】耐久条件

エンジン4400ccの排気系に触媒を装着し、触媒入口温度700℃で、50時間運転して耐久を行った。

【0068】評価条件

触媒活性評価は、排気量2000ccのエンジンの排気系に各触媒を装着し、A/F=14.6（ストイキ状態）で60秒間、その後A/F=2.2（リーン雰囲気）＊

＊で10秒間、その後A/F=5.0（リーン雰囲気）で10秒間の運転を1サイクル行ない、各々平均転化率を測定し、このA/F=14.6（ストイキ状態）の場合の平均転化率とA/F=2.2（リーン雰囲気）の場合の平均転化率とA/F=5.0（リーン雰囲気）の場合の平均転化率とを平均してトータル転化率とした。この評価を初期及び耐久後に各々行ない、触媒活性評価値を以下の式により決定した。但し触媒入口温度を350℃とした。

【0069】

【数4】

$$\text{NOx転化率(\%)} = \frac{[\text{触媒入口NOx濃度}] - [\text{触媒出口NOx濃度}]}{[\text{触媒入口NOx濃度}]} \times 100$$

（HC、COも同様）

【0070】トータル転化率として得られた触媒活性評価結果を表2に示す。比較例に比べて実施例は、触媒活性が高く、後述する本発明の効果を確認することができた。

【0071】

【表2】

13

評価結果

	転化率 %					
	初 期			耐 久 後		
	HC	CO	NO _x	HC	CO	NO _x
実施例 1	97	99	90	96	98	80
実施例 2	98	99	88	95	98	76
実施例 3	97	99	89	95	98	78
実施例 4	97	99	89	94	96	73
比較例 1	98	99	82	96	93	60
比較例 2	98	99	85	96	98	70
比較例 3	97	99	89	92	96	60
比較例 4	97	99	89	96	96	69
比較例 5	97	99	90	96	98	82
比較例 6	98	99	82	96	98	59
比較例 7	98	99	80	96	93	50

(8)

特開2000-279814

14

*【0072】

【発明の効果】請求項1～5記載の排気ガス浄化用触媒は、従来の触媒では十分な活性を示さなかったリーン雰囲気下におけるNO_x浄化性能を向上させ、かつ三元触媒としての機能を十分に発現することができ、更に熱耐久後においても優れたNO_x浄化性能を示すことができる。

【0073】請求項6及び7記載の排気ガス浄化用触媒の使用方法は、上記本発明の排気ガス浄化用触媒の有効なNO_x吸収、放出サイクルを特に効率良く発現させることができる。

*

フロントページの続き

Fターム(参考) 4D048 AA02 AA06 AA13 BA08X
 BA18X BA30X BA31X BA33X
 BA42X BB01 BB17 CC62
 4G059 AA01 AA02 AA15 BA01A
 BA01B BA13B BB06A BB06B
 BC42A BC42B BC44A BC51A
 BC51B BC71A BC72A BC72B
 BC75A CA03 CA09 CA13
 EA02X EA02Y EA19 EB18X
 EB18Y EC23 EE05

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-279814

(43)Date of publication of application : 10. 10. 2000

(51) Int. Cl.

B01J 23/63

B01D 53/86

B01D 53/94

(21)Application number : 11-092105

(71)Applicant : NISSAN MOTOR CO LTD

(22)Date of filing : 31. 03. 1999

(72)Inventor : HANAKI YASUNARI
SUGA KATSUO

(54) EXHAUST GAS CLEANING CATALYST AND ITS USE

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance NO_x cleaning capacity under a lean atmosphere and to sufficiently develop the function as a ternary catalyst by adding at least one noble metal selected from the group consisting of platinum, palladium and rhodium and composite oxide represented by a specific formula.

SOLUTION: An exhaust gas cleaning catalyst contains at least one noble metal selected from the group consisting of platinum, palladium and rhodium and composite oxide represented by the formula $\text{Ln}\alpha\text{Zr}_{1-\alpha}\text{O}_x$ (wherein α is $0.4 < \alpha < 0.9$, x is an oxygen amt. satisfying valencies of respective atoms and Ln is at least one element selected from the group consisting of La, Pr and Nd). Composite oxide to be used contains a rare earth metal and a transition metal and avoids the compounding of a rare earth metal with alumina and facilitates the adsorption of NO_x even after endurance and utilizes characteristics absorbing NO_x in a lean atmosphere to enhance NO_x cleaning capacity.

* NOTICES *

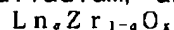
JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] At least a kind of precious metals chosen from a group which comprises platinum, palladium, and rhodium, and the following general formula [Equation 1]



(式中、0.4 < α < 0.9、xは各原子の価数を満足する酸素量、

$L_n = La, Pr$ 及び Nd から成る群より選ばれた少なくとも一種を示す)

The catalyst for exhaust gas purification coming out and containing the perovskite type multiple oxide expressed.

[Claim 2] The catalyst for exhaust gas purification according to claim 1 containing catalyst 1 for exhaust gas purification L per 30-100g of multiple oxides.

[Claim 3] The catalyst for exhaust gas purification according to claim 1 or 2 containing catalyst 1 L per 100-300g of alumina for the exhaust gas above.

[Claim 4] claims 1-3 which provide a layer which does not contain the above-mentioned multiple oxide in a lower layer for a layer which comprises structure which provided two-layer at least on an inorganic carrier, and contains the above-mentioned multiple oxide in the upper layer, and are characterized by things -- a catalyst for exhaust gas purification given [one of] in a paragraph.

[Claim 5] claims 1-4, wherein mean particle diameter of material which constitutes a catalyst bed is 4 micrometers or less -- a catalyst for exhaust gas purification given [one of] in a paragraph.

[Claim 6] claims 1-5 -- the directions for a catalyst for exhaust gas purification, wherein an air-fuel ratio uses a catalyst for exhaust gas purification given [one of] in a paragraph for a lean burn engine car which repeats the range of 10-50.

[Claim 7] claims 1-5 -- the directions for a catalyst for exhaust gas purification, wherein an air-fuel ratio uses a catalyst for exhaust gas purification given [one of] in a paragraph for a lean burn engine car which repeats 10-14.8, and the range of 15-50.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Hydrocarbon (HC) in the exhaust gas with which this invention is discharged from internal-combustion engines, such as a car and a boiler, It is related with a catalyst for exhaust gas purification which is especially excellent in the purification performance of NO_x under hyperoxia atmosphere, and directions for use for the same about a catalyst for exhaust gas purification which purifies carbon monoxide (CO) and nitrogen oxides (NO_x), and directions for use for the same.

[0002]

[Description of the Prior Art]The three way component catalyst which performs oxidation of CO and HC and reduction of NO_x simultaneously, and purifies exhaust gas as a catalyst for exhaust gas purification of a car conventionally is used. As a three way component catalyst, a supporting layer is formed in fireproof carriers, such as cordierite, from gamma-alumina etc., for example, and the thing which made the supporting layer support precious metal catalysts, such as Pt, Pd, and Rh, is known widely.

[0003]The purification performance of such a catalyst for exhaust gas purification changes greatly with engine air-fuel ratios (A/F). That is, in the Lean side with thin fuel concentration whose air-fuel ratio is large, the amount of oxygen in exhaust gas increases, and while the oxidation reaction which purifies CO and HC is active, the reduction reaction which purifies NO_x becomes inertness. Conversely, small [an air-fuel ratio] that is, by a rich side with deep fuel concentration, the amount of oxygen in exhaust gas decreases, and although oxidation reaction serves as inertness, a reduction reaction becomes active.

[0004]On the other hand, in a run of a car, in an urban area run, start and a stop are performed frequently, and an air-fuel ratio changes frequently by within the limits from [near the theoretical value] to an exaggerated RIN state. In order to respond to the request of low-fuel-consumption-izing in such a run, operation by the side of Lean who supplies the gaseous mixture of hyperoxia if possible is needed. Therefore, development of the catalyst which can fully purify NO_x to the Lean side is desired.

[0005]Various catalysts which raise the NO_x purification performance under lean atmosphere from before are proposed, for example, platinum (Pt) is made to support a lantern etc. to JP, 5-168860, A, and the catalyst using a lantern as a NO_x absorber is indicated. This absorbs NO_x under lean atmosphere and carries out discharge purification of the NO_x under a SUTOIKI state or overfuel (rich) atmosphere.

[0006]However, the above-mentioned conventional NO_x absorption catalyst (for example, Pt-lantern catalyst), When a regular run is performed by lean atmosphere, a NO_x absorbed amount reaches saturation, there is a problem that absorption disappears soon on the characteristic, NO_x purification performance runs short, and the performance after durability cannot be enough, either and cannot purify NO_x under a broad operating condition.

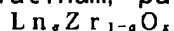
[0007]

[Problem(s) to be Solved by the Invention]Therefore, the purpose of the invention according to claim 1 to 5 is to provide the catalyst for exhaust gas purification which can raise the NO_x purification performance under the lean atmosphere which did not show activity sufficient with the conventional catalyst, and can fully reveal the function as a three way component catalyst.

[0008]The purpose of the invention according to claim 6 or 7 has the NO_x cleaning effect of the catalyst for exhaust gas purification of this invention in providing the directions for the catalyst for exhaust gas purification which can be revealed especially effectively.

[0009]

[Means for Solving the Problem]At least a kind of precious metals chosen from a group to which the catalyst for exhaust gas purification according to claim 1 changes from platinum, palladium, and rhodium, and the following general formula [Equation 2]



(式中、0.4 < α < 0.9、xは各原子の価数を満足する酸素量、

L_n = L_a, P_r及びN_dから成る群より選ばれた少なくとも一種

を示す)

It comes out and the multiple oxide expressed is contained.

[0010]In the catalyst for exhaust gas purification according to claim 1, a multiple oxide contains catalyst 1for exhaust gas purification L per 30-100g of the catalysts for exhaust gas purification according to claim 2.

[0011]The catalyst for exhaust gas purification according to claim 3 contains catalyst 1L per 100-300g of alumina for the exhaust gas above further in the catalyst for exhaust gas purification according to claim 1 or 2.

[0012]the catalyst for exhaust gas purification according to claim 4 — claims 1-3 — in the catalyst for exhaust gas purification given [one of] in a paragraph, the structure which provided two-layer at least on the inorganic carrier is comprised, and the layer which does not contain the above-mentioned multiple oxide in a lower layer for the layer containing the above-mentioned multiple oxide is provided in the upper layer

[0013]the catalyst for exhaust gas purification according to claim 5 — claims 1-4 — in a catalyst for exhaust gas purification given [one of] in a paragraph, it is characterized by mean particle diameter of material which constitutes a catalyst bed being 4 micrometers or less.

[0014]In order to make effective NO_x absorption of a catalyst for exhaust gas purification of above-mentioned this invention, and a discharge cycle reveal, the directions for the catalyst for exhaust gas purification according to claim 6, Empty fuel consumption uses a catalyst for exhaust gas purification of this invention for a lean burn engine car which repeats the range of 10-50.

[0015]the catalyst for exhaust gas purification according to claim 7 — claims 1-5 — an air-fuel ratio uses a catalyst for exhaust gas purification given [one of] in a paragraph for a lean burn engine car which repeats 10-14.8, and the range of 15-50

[0016]

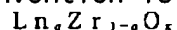
[Embodiment of the Invention]At least one sort chosen from the group which comprises platinum, palladium, and rhodium is used for the precious metals in the catalyst for exhaust gas purification of this invention. For example, various combination of Pt, Rh, Pd, Rh, Pd, etc., etc. is possible. The content of said precious metals will not be limited especially if NO_x absorption power and three way component catalyst performance are fully obtained, but. As for the significant improvement in the characteristic, if less than 0.1 g, even if the performance of 3 sufficient yuan will not be obtained but it will use it mostly from 10 g, per [which are not seen / catalyst 1L for exhaust gas

purification of a point to this invention / 0.1-10g] are preferred.

[0017] Since the catalyst of this invention also needs the function as a three way component catalyst at the time of SUTOIKI, as for the above-mentioned precious metals, it is preferred that at least a part is supported by the porous body of an inorganic carrier, and being supported by especially alumina is preferred. The heat-resistant high thing of the alumina used here is preferred, and its specific surface area is [activated alumina of 50-300 m²/g] especially preferred. In order to raise the heat resistance of alumina, additives, such as rare earth compounds, such as cerium and a lanthanum, and a zirconium, may be further added as applied with the three way component catalyst from the former. As for the content, it is preferred to consider it as per [catalyst 1L for exhaust gas purification / 100-300g] from the point that NO_x oxidation activity which also needs that of the precious metals, especially Pd for NO_x absorption reaction is demonstrated to the maximum extent.

[0018] Since the catalyst used by this invention also needs the function as a three way component catalyst at the time of SUTOIKI, They are Series which may add further the additive used with the three way component catalyst from the former, for example, has an oxygen storage function, barium which eases HC adsorption poisoning to the precious metals, the zirconia which contributes to the improvement in heat-resistant of Rh, etc.

[0019] The multiple oxide contained in the catalyst for exhaust gas purification of this invention is the following general formula. [Equation 3]



(式中、0.4 < α < 0.9、xは各原子の価数を満足する酸素量、

L n = La, Pr及びNdから成る群より選ばれた少なくとも一種

を示す)

It is come out and expressed.

[0020] A rare earth metal and a transition metal are contained in a multiple oxide used for a catalyst for exhaust gas purification of this invention. As a rare earth metal, a lanthanum, praseodymium, and neodymium can use it, and a zirconium can use it conveniently as a transition metal.

[0021] Such a multiple oxide can raise purification performance of NO_x by avoiding composite-ization with a rare earth metal and alumina by adsorption of NO_x becoming easy also after durability and using the characteristic of absorbing NO_x in lean atmosphere.

[0022] If a value of alpha is 0.9 or more, it is equivalent to an independent oxide of a rare earth metal. Since NO adsorption capacity which a rare earth element has will fall and sufficient NO_x purification performance will not be obtained if it is 0.4 or less, it is preferred that it is 0.4 < alpha < 0.9. A value of x is the amount of oxygen with which it is satisfied of a valence of each atom, and is about about 0 < delta < 4.

[0023] When at least one sort chosen from a group which comprises a lanthanum, praseodymium, and neodymium forms a Zr and perovskite type multiple oxide, composite-ization of these rare earth metals and alumina is avoided, and NO_x adsorption becomes easy also after durability. When a multiple oxide is not formed, if La₂O₃ and ZrO₂ were mixed, after durability, NO_x adsorption performance will fall greatly especially, for example.

[0024] Although a multiple oxide used by this invention makes performance which absorbs NO_x under lean atmosphere reveal, NO_x in the gaseous phase oxidizes to NO₂ on the precious metals, it serves as NO₃ further on a multiple oxide, and the absorber style is absorbed on a multiple oxide. Therefore, it is important for a presentation of a multiple oxide for absorbing NO_x effectively under lean atmosphere to have contained at least one sort of elements chosen from a group which comprises La and Pr which have the operation of being

easy to make NO_3 salt, and Nd, and to have composite-sized with Zr.

[0025]When these all that are contained in a catalyst have composite-sized each composing element of this multiple oxide, the above-mentioned operation is demonstrated to the maximum extent, but even when at least a part can form a complex, the above-mentioned operation can fully be obtained.

[0026]Each composing element of this multiple oxide can exist as a multiple oxide, without dissociating as a separate oxide also after heat durability, and this can be checked for example, by X diffraction measurement.

[0027]It is hafnium, sulfur, etc. which are contained in strontium which may contain a small amount of impurities in each composing element in this multiple oxide as long as it is not the quantity which bars the above-mentioned operation, for example, is contained in barium, cerium contained in a lantern, neodymium, samarium, or a zirconium.

[0028]If quantity from which the operation is obtained contains said multiple oxide powder in a catalyst, although content in particular is not limited, its thing for exhaust gas purification containing catalyst 1L per 30-100g of this invention is preferred from a point of obtaining enough and significant NO_x absorption.

[0029]The catalyst for exhaust gas purification of this invention can acquire a NO_x cleaning effect which is not acquired if respectively independent by making said precious metals and a multiple oxide live together. That is, when exhaust gas atmosphere becomes Lean, high NO_x purification performance is obtained by NO_x absorption by a multiple oxide in a catalyst for exhaust gas purification of this invention. If this multiple oxide carries out NO_x absorption and exhaust gas atmosphere changes from Lean to SUTOIKI, NO_x will be emitted from this multiple oxide and high NO_x purification performance will be obtained. NO_x purification performance which was not obtained only by mixing an independent thing of each ingredient which constitutes this multiple oxide, and was excellent is obtained.

[0030]Other catalysts for exhaust gas purification of this invention comprise structure which provided two-layer at least on a fireproof inorganic carrier, and provide a layer which does not contain the above-mentioned multiple oxide in a lower layer for a layer containing the above-mentioned multiple oxide in the upper layer.

[0031]Thus, it will multilayer-structure-size, and NO_x emitted at SUTOIKI - the time of rich can be efficiently purified by making a inner layer contain a multiple oxide, and a fall of HC purification function of the three way component catalyst functions can be controlled. Namely, it is good to arrange in the upper layer which does not contain a multiple oxide, in order to purify discharge NO_x effectively, By considering it as such a structure, NO_x will be absorbed by a inner layer containing a multiple oxide, discharge NO_x will be purified in the upper layer which does not contain a multiple oxide, and still more sufficient three way component catalyst function can be obtained.

[0032]As for mean particle diameter (median size) of material which constitutes a catalyst bed of this invention, it is preferred that it is 4 micrometers or less. By making particle diameter into such a range, NO_x absorptance at the time of Lean can be raised.

[0033]That is, NO_x absorption which was excellent when a catalyst for exhaust gas purification made gas flow speed late can be demonstrated, and such an effect is attained by considering it as mean particle diameter of a mentioned range, and, as a result, can acquire high NO_x absorption activity.

[0034]By considering it as this mean particle diameter, the desirable precious metals supported suitably in an exhaust gas catalyst of this invention can be high-decentralized, and NO_x absorption can also be raised.

[0035]As for mean particle diameter, in order to raise said effect further especially, it is preferred that it is 2-4 micrometers. Mean particle diameter in this specification is measured with a laser diffraction type particle-size-distribution meter.

[0036]After it mixes to composition ratio of a multiple oxide for which it asks and a

multiple oxide used for this invention carries out temporary calcination of a nitrate of each composing element of a multiple oxide, acetate, carbonate, citrate, the hydrochloride, etc., it is ground, A nitrate of solid phase reaction which carries out heat treatment calcination, and each composing element of a multiple oxide, acetate, Carbonate, a hydrochloride, citrate, etc. are mixed to composition ratio of a multiple oxide for which it asks, After dissolving in water, can prepare with a coprecipitation method which trickles alkali solutions, such as NH_4OH and NH_3CO_3 , if needed, is made to dry a postprecipitation neutralized precipitate which generated and filtered a sediment, and is calcinated, but. It is not limited to these methods and a multiple oxide should just be formed also by a method except said.

[0037]By this method, at least a part of each ingredient which constitutes a multiple oxide can be composite-sized.

[0038]It is hafnium, sulfur, etc. which are contained in cerium, neodymium and samarium which may contain a small amount of impurities in a raw material for catalyst preparation of a multiple oxide used by this invention as long as it is not the quantity which bars the above-mentioned operation, as described above, for example, are contained in a rare earth metal, and a zirconium.

[0039]Although it can be used combining an inorganic acid salt, carbonate, ammonium salt, organic acid salt, a halogenide, an oxide, sodium salt, an ammine complex compound, etc. as a precious-metals raw material compound of the precious metals used for this invention, It is preferred to use a water-soluble salt especially from a viewpoint of raising catalyst performance. Unless it is not limited to a method special as a method of supporting a porous body of the precious metals but is accompanied by remarkable maldistribution of an ingredient, various methods, such as the publicly known evaporating method, a sedimentation method, the impregnating method, and an ionic exchange method, can be used. A point which improves dispersibility to especially support to alumina to the impregnating method is preferred.

[0040]When based on an ionic exchange method and the impregnating method, since a metallic raw material is used with a solution in many cases, it can add acid or a base in the solution, and can also adjust pH. By adjusting pH, high distribution support may be able to be carried out further.

[0041]A catalyst for exhaust gas purification of this invention can be acquired by it being preferred to support and use for an integral-construction type carrier as for a catalyst of this invention, and grinding a multiple oxide and a precious-metals support inorganic carrier, considering it as a slurry, carrying out a coat to catalyst support, and calcinating at temperature of 400-900 **.

[0042]A grinding method in particular of hitting grinding a multiple oxide and a precious-metals support inorganic carrier cannot be limited, but can carry out the wet milling of the aqueous slurry which contains these preferably, and can use a method of adjusting so that mean particle diameter may be set to 4 micrometers or less.

[0043]A device in particular that can be used for grinding is not limited, but can use a commercial ball type vibration mill, adjusts a ball diameter, grinding time, amplitude, and vibrational frequency, and obtains desired particle diameter.

[0044]A honeycomb carrier, a metal carrier, etc. which have the monolith structure which can use it choosing suitably from publicly known catalyst support as catalyst support for example, which consists of a fireproof material are mentioned.

[0045]Although many things of quality of cordierite, such as ceramics, are used generally [although not restricted / it is preferred to usually use it with honeycomb shape, and] as this honeycomb material, especially shape of this catalyst support, It is also possible to use a honeycomb which consists of metallic materials, such as ferrite series stainless steel, and also the catalyst powder itself may be fabricated to honeycomb shape. By making shape of a catalyst into honeycomb shape, since a catalyst-surfaces product of a catalyst

and exhaust gas becomes large and pressure loss is also suppressed, when using as an object for cars, etc., it is very advantageous.

[0046] Although a catalyst for exhaust gas purification in particular of above-mentioned this invention does not have the service condition limited, an air-fuel ratio can use it for 10-50, and a lean burn engine car by which an air-fuel ratio repeats 10-14.8, and the range of 15-50 still more preferably preferably. By considering it as such directions for use, a cycle of NO_x absorption and discharge is materialized very effectively, and NO_x purification especially with sufficient efficiency of it is attained. Namely, by an air-fuel ratio's absorbing NO_x in a field (lean area) where an air-fuel ratio of 10-50 within the limits is big, and purifying NO_x in a field (rich and/or SUTOIKI) where an air-fuel ratio is small, High NO_x purification performance can be obtained and fields of a still more suitable range where 10 to 14.8 and an air-fuel ratio have a big field where an air-fuel ratio is small are 15-50.

[0047]

[Example] Hereafter, a following example and comparative example explain this invention. Activated alumina powder was impregnated, example 1 nitric-acid Pd solution was calcinated at 400 ** after desiccation and among the air for 1 hour, and Pd support alumina powder (powder 1) was obtained. Pd concentration of this powder 1 was 2.8 % of the weight.

Activated alumina powder was impregnated, dinitrodiamine Pt solution was calcinated at 400 ** after desiccation and among the air for 1 hour, and Pt support alumina powder (powder 2) was obtained. Pd concentration of this powder 2 was 2.8 % of the weight. Activated alumina powder was impregnated, nitric acid Rh solution was calcinated at 400 ** after desiccation and among the air for 1 hour, and Rh support alumina powder (powder 3) was obtained. Rh concentration of this powder 3 was 0.7 % of the weight.

[0048] Citrate was added to lantern carbonate and the mixture of the zirconium nitrate, it calcinated at 700 ** after desiccation, and La-Zr multiple oxide powder (powder 4) was obtained. This powder 4 was lantern/zirconium =5/5 in the metal atom ratio.

[0049] 90 g and the above-mentioned powder 4 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 180 g and the above-mentioned powder 2 was carried out for the above-mentioned powder 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having made this slurry liquid adhere to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (A) of the coated layer weight [of 125 g/L]-carrier was acquired.

[0050] 90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the above-mentioned powder 2 was carried out for the above-mentioned powder 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having made this slurry liquid adhere to the above-mentioned catalyst (A), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 250 g/L]-carrier was acquired.

[0051] The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having replaced La of the example 2 powder 4 with Nd.

[0052] The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having replaced La of the example 3 powder 4 with Pr.

[0053] 180 g and the powder 4 were thrown into 180 g, the water 720g was fed into the magnetic ball mill, preferential grinding of 180 g and the powder 2 was carried out [the powder 1 obtained in example 4 Example 1] for 180 g and the powder 3, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having made this slurry liquid adhere to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at

130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the coated layer weight [of 250 g/L]-carrier was acquired.

[0054]The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having used the activated alumina powder which did 6 mol% addition of La instead except for the comparative example 1 powder 4.

[0055]The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having prepared the mean particle diameter of comparative example 2 slurry to 8 micrometers.

[0056]90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in comparative example 3 Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (B) of the coated layer weight [of 125 g/L]-carrier was acquired.

[0057]90 g and the powder 4 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the catalyst (B), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 250 g/L]-carrier was acquired.

[0058]60 g and activated alumina were thrown into 120 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out [the powder 1 obtained in comparative example 4 Example 1] for 90 g and the powder 4, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (C) of the coated layer weight [of 125 g/L]-carrier was acquired.

[0059]90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the catalyst (C), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 250 g/L]-carrier was acquired.

[0060]90 g and the powder 4 were thrown into 360 g, the water 540g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in comparative example 5 Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (D) of the coated layer weight [of 187.5 g/L]-carrier was acquired.

[0061]90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the catalyst (D), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 312.5 g/L]-carrier was acquired.

[0062] In comparative example 6 Example 1, except having used La_2O_3 45g ZrO_2 135g instead of the powder 4, it is the same method as Example 1, and the catalyst for exhaust gas purification was acquired.

[0063] In comparative example 7 Example 1, except that the ratio of La to Zr set the powder 4 to $\text{La/Zr}=1/9$, it is the same method and the catalyst for exhaust gas purification was acquired.

[0064] The catalyst presentation of the catalyst for exhaust gas purification acquired by said Examples 1-4 and the comparative examples 1-7 is shown in Table 1.

[0065]

[Table 1]
組 成 表

	貴金属(g/L)			コ-ト層構造	複合酸化物の位置	複合酸化物量(g)	スラリー粒径	複合酸化物組成
	Pt	Pd	Rh					
実施例 1	1.75	1.75	0.43	2層	下層	180	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
実施例 2	1.75	1.75	0.43	2層	下層	180	$2.8\mu\text{m}$	$\text{Nd}_{0.5}\text{Zr}_{0.5}\text{O}_x$
実施例 3	1.75	1.75	0.43	2層	下層	180	$2.8\mu\text{m}$	$\text{Pr}_{0.5}\text{Zr}_{0.5}\text{O}_x$
実施例 4	1.75	1.75	0.43	1層	—	180	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 1	1.75	1.75	0.43	2層	下層	180	$2.8\mu\text{m}$	$\text{La}6\text{mol}\%\text{-Al}_2\text{O}_3$
比較例 2	1.75	1.75	0.43	2層	下層	180	$8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 3	1.75	1.75	0.43	2層	上層	180	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 4	1.75	1.75	0.43	2層	下層	60	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 5	1.75	1.75	0.43	2層	下層	360	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 6	1.75	1.75	0.43	2層	—	La_2O_3 45g ZrO_2 135g	$2.8\mu\text{m}$	$\text{La}_2\text{O}_3+\text{ZrO}_2$
比較例 7	1.75	1.75	0.43	2層	下層	180	$2.8\mu\text{m}$	$\text{La}_{0.1}\text{Zr}_{0.9}\text{O}_x$

[0066] About the catalyst for exhaust gas purification acquired by the example of examination aforementioned examples 1-4, and the comparative examples 1-7, catalytic activity evaluation after the first stage and durability was performed on condition of the following. The automatic evaluation device using the model gas which imitated the exhaust gas of the car was used for activity evaluation.

[0067] The durable condition engine 4400cc exhaust system was equipped with the catalyst, with the catalyst inlet temperature of 700 **, it operated for 50 hours and durability was performed.

[0068] Evaluation condition catalytic activity evaluation equips the exhaust system of an engine with a displacement of 2000 cc with each catalyst, After that for 60 seconds by $\text{A/F}=14.6$ (SUTOIKI state) $\text{A/F}=22$ (lean atmosphere) For 10 seconds, After that operation for 10 seconds by $\text{A/F}=50$ (lean atmosphere) 1 cycle deed, The average inversion rate was measured respectively, the average inversion rate in this $\text{A/F}=14.6$ (SUTOIKI state), the average inversion rate in $\text{A/F}=22$ (lean atmosphere), and the average inversion rate in $\text{A/F}=50$ (lean atmosphere) were averaged, and it was considered as the total inversion rate. This evaluation was respectively performed after the first stage and durability, and the

following formulas determined the catalytic activity evaluation value. However, catalyst inlet temperature was 350 **.

[0069]

[Equation 4]

$$\text{NOx 転化率(\%)} = \frac{[\text{触媒層入口NOx濃度}] - [\text{触媒層出口NOx濃度}]}{[\text{触媒層入口NOx濃度}]} \times 100$$

(HC, CO も同様)

[0070] The catalytic activity evaluation result obtained as a total inversion rate is shown in Table 2. Compared with the comparative example, catalytic activity of the example was high, and the effect of this invention mentioned later was able to be checked.

[0071]

[Table 2]

評価結果

	転化率 %					
	初期			耐久後		
	HC	CO	NOx	HC	CO	NOx
実施例 1	97	99	90	96	98	80
実施例 2	98	99	88	95	98	76
実施例 3	97	99	89	95	98	78
実施例 4	97	99	89	94	96	73
比較例 1	98	99	82	96	98	60
比較例 2	98	99	85	96	98	70
比較例 3	97	99	89	92	96	60
比較例 4	97	99	89	96	96	69
比較例 5	97	99	90	96	98	82
比較例 6	98	99	82	96	98	59
比較例 7	98	99	80	96	98	50

[0072]

[Effect of the Invention] The catalyst for exhaust gas purification according to claim 1 to 5 can raise the NOx purification performance under the lean atmosphere which did not show activity sufficient with the conventional catalyst, the function as a three way component catalyst can fully be revealed, and also the NOx purification performance outstanding after heat durability can be shown.

[0073] The directions for the catalyst for exhaust gas purification given in claims 6 and 7 can make effective NOx absorption of the catalyst for exhaust gas purification of above-mentioned this invention, and a discharge cycle reveal efficiently especially.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention]Hydrocarbon (HC) in the exhaust gas with which this invention is discharged from internal-combustion engines, such as a car and a boiler, It is related with a catalyst for exhaust gas purification which is especially excellent in the purification performance of NOx under hyperoxia atmosphere, and directions for use for the same about a catalyst for exhaust gas purification which purifies carbon monoxide (CO) and nitrogen oxides (NOx), and directions for use for the same.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art]The three way component catalyst which performs oxidation of CO and HC and reduction of NOx simultaneously, and purifies exhaust gas as a catalyst for exhaust gas purification of a car conventionally is used. As a three way component catalyst, a supporting layer is formed in fireproof carriers, such as cordierite, from gamma-alumina etc., for example, and the thing which made the supporting layer support precious metal catalysts, such as Pt, Pd, and Rh, is known widely.

[0003]The purification performance of such a catalyst for exhaust gas purification changes greatly with engine air-fuel ratios (A/F). That is, in the Lean side with thin fuel concentration whose air-fuel ratio is large, the amount of oxygen in exhaust gas increases, and while the oxidation reaction which purifies CO and HC is active, the reduction reaction which purifies NOx becomes inertness. Conversely, small [an air-fuel ratio] that is, by a rich side with deep fuel concentration, the amount of oxygen in exhaust gas decreases, and although oxidation reaction serves as inertness, a reduction reaction becomes active.

[0004]On the other hand, in a run of a car, in an urban area run, start and a stop are performed frequently, and an air-fuel ratio changes frequently by within the limits from [near the theoretical value] to an exaggerated RIN state. In order to respond to the request of low-fuel-consumption-izing in such a run, operation by the side of Lean who supplies the gaseous mixture of hyperoxia if possible is needed. Therefore, development of the catalyst which can fully purify NOx to the Lean side is desired.

[0005]Various catalysts which raise the NOx purification performance under lean atmosphere from before are proposed, for example, platinum (Pt) is made to support a lantern etc. to JP, 5-168860, A, and the catalyst using a lantern as a NOx absorber is indicated. This absorbs NOx under lean atmosphere and carries out discharge purification of the NOx under a SUTOIKI state or overfuel (rich) atmosphere.

[0006]However, the above-mentioned conventional NOx absorption catalyst (for example, Pt-lantern catalyst), When a regular run is performed by lean atmosphere, a NOx absorbed amount reaches saturation, there is a problem that absorption disappears soon on the characteristic, NOx purification performance runs short, and the performance after durability cannot be enough, either and cannot purify NOx under a broad operating condition.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention]The catalyst for exhaust gas purification according to claim 1 to 5 can raise the NOx purification performance under the lean atmosphere which did not show activity sufficient with the conventional catalyst, the function as a three way component catalyst can fully be revealed, and also the NOx purification performance outstanding after heat durability can be shown.

[0073]The directions for the catalyst for exhaust gas purification given in claims 6 and 7 can make effective NOx absorption of the catalyst for exhaust gas purification of above-mentioned this invention, and a discharge cycle reveal efficiently especially.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Therefore, the purpose of the invention according to claim 1 to 5 is to provide the catalyst for exhaust gas purification which can raise the NO_x purification performance under the lean atmosphere which did not show activity sufficient with the conventional catalyst, and can fully reveal the function as a three way component catalyst.

[0008] The purpose of the invention according to claim 6 or 7 has the NO_x cleaning effect of the catalyst for exhaust gas purification of this invention in providing the directions for the catalyst for exhaust gas purification which can be revealed especially effectively.

[Translation done.]

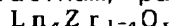
* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] At least a kind of precious metals chosen from a group to which the catalyst for exhaust gas purification according to claim 1 changes from platinum, palladium, and rhodium, and the following general formula [Equation 2]



(式中、0.4 < α < 0.9、xは各原子の価数を満足する酸素量、

L_n = La, Pr及びNdから成る群より選ばれた少なくとも一種

を示す)

It comes out and the multiple oxide expressed is contained.

[0010] In the catalyst for exhaust gas purification according to claim 1, a multiple oxide contains catalyst 1 for exhaust gas purification L per 30-100g of the catalysts for exhaust gas purification according to claim 2.

[0011] The catalyst for exhaust gas purification according to claim 3 contains catalyst 1L per 100-300g of alumina for the exhaust gas above further in the catalyst for exhaust gas purification according to claim 1 or 2.

[0012] the catalyst for exhaust gas purification according to claim 4 -- claims 1-3 -- in the catalyst for exhaust gas purification given [one of] in a paragraph, the structure which provided two-layer at least on the inorganic carrier is comprised, and the layer which does not contain the above-mentioned multiple oxide in a lower layer for the layer containing the above-mentioned multiple oxide is provided in the upper layer

[0013] the catalyst for exhaust gas purification according to claim 5 -- claims 1-4 -- in a catalyst for exhaust gas purification given [one of] in a paragraph, it is characterized by mean particle diameter of material which constitutes a catalyst bed being 4 micrometers or less.

[0014] In order to make effective NO_x absorption of a catalyst for exhaust gas purification of above-mentioned this invention, and a discharge cycle reveal, the directions for the catalyst for exhaust gas purification according to claim 6, Empty fuel consumption uses a catalyst for exhaust gas purification of this invention for a lean burn engine car which repeats the range of 10-50.

[0015] the catalyst for exhaust gas purification according to claim 7 -- claims 1-5 -- an air-fuel ratio uses a catalyst for exhaust gas purification given [one of] in a paragraph for a lean burn engine car which repeats 10-14.8, and the range of 15-50

[0016]

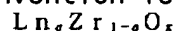
[Embodiment of the Invention] At least one sort chosen from the group which comprises platinum, palladium, and rhodium is used for the precious metals in the catalyst for exhaust gas purification of this invention. For example, various combination of Pt, Rh, Pd, Rh, Pd, etc., etc. is possible. The content of said precious metals will not be limited especially if NO_x absorption power and three way component catalyst performance are fully obtained, but. As for the significant improvement in the characteristic, if less

than 0.1 g, even if the performance of 3 sufficient yuan will not be obtained but it will use it mostly from 10 g, per [which are not seen / catalyst 1L for exhaust gas purification of a point to this invention / 0.1-10g] are preferred.

[0017] Since the catalyst of this invention also needs the function as a three way component catalyst at the time of SUTOIKI, as for the above-mentioned precious metals, it is preferred that at least a part is supported by the porous body of an inorganic carrier, and being supported by especially alumina is preferred. The heat-resistant high thing of the alumina used here is preferred, and its specific surface area is [activated alumina of 50-300 m²/g] especially preferred. In order to raise the heat resistance of alumina, additives, such as rare earth compounds, such as cerium and a lanthanum, and a zirconium, may be further added as applied with the three way component catalyst from the former. As for the content, it is preferred to consider it as per [catalyst 1L for exhaust gas purification / 100-300g] from the point that NO_x oxidation activity which also needs that of the precious metals, especially Pd for NO_x absorption reaction is demonstrated to the maximum extent.

[0018] Since the catalyst used by this invention also needs the function as a three way component catalyst at the time of SUTOIKI, They are Seria which may add further the additive used with the three way component catalyst from the former, for example, has an oxygen storage function, barium which eases HC adsorption poisoning to the precious metals, the zirconia which contributes to the improvement in heat-resistant of Rh, etc.

[0019] The multiple oxide contained in the catalyst for exhaust gas purification of this invention is the following general formula. [Equation 3]



(式中、0.4 < α < 0.9、xは各原子の価数来满足する酸素量、

L_n = La, Pr及びNdから成る群より選ばれた少なくとも一種

を示す)

It is come out and expressed.

[0020] A rare earth metal and a transition metal are contained in a multiple oxide used for a catalyst for exhaust gas purification of this invention. As a rare earth metal, a lanthanum, praseodymium, and neodymium can use it, and a zirconium can use it conveniently as a transition metal.

[0021] Such a multiple oxide can raise purification performance of NO_x by avoiding composite-ization with a rare earth metal and alumina by adsorption of NO_x becoming easy also after durability and using the characteristic of absorbing NO_x in lean atmosphere.

[0022] If a value of alpha is 0.9 or more, it is equivalent to an independent oxide of a rare earth metal. Since NO adsorption capacity which a rare earth element has will fall and sufficient NO_x purification performance will not be obtained if it is 0.4 or less, it is preferred that it is 0.4 < alpha < 0.9. A value of x is the amount of oxygen with which it is satisfied of a valence of each atom, and is about about 0 < delta < 4.

[0023] When at least one sort chosen from a group which comprises a lanthanum, praseodymium, and neodymium forms a Zr and perovskite type multiple oxide, composite-ization of these rare earth metals and alumina is avoided, and NO_x adsorption becomes easy also after durability. When a multiple oxide is not formed, if La₂O₃ and ZrO₂ were mixed, after durability, NO_x adsorption performance will fall greatly especially, for example.

[0024] Although a multiple oxide used by this invention makes performance which absorbs NO_x under lean atmosphere reveal, NO_x in the gaseous phase oxidizes to NO₂ on the precious metals, it serves as NO₃ further on a multiple oxide, and the absorber style is absorbed on a multiple oxide. Therefore, it is important for a presentation of a multiple oxide for

absorbing NO_x effectively under lean atmosphere to have contained at least one sort of elements chosen from a group which comprises La and Pr which have the operation of being easy to make NO₃ salt, and Nd, and to have composite-sized with Zr.

[0025]When these all that are contained in a catalyst have composite-sized each composing element of this multiple oxide, the above-mentioned operation is demonstrated to the maximum extent, but even when at least a part can form a complex, the above-mentioned operation can fully be obtained.

[0026]Each composing element of this multiple oxide can exist as a multiple oxide, without dissociating as a separate oxide also after heat durability, and this can be checked for example, by X diffraction measurement.

[0027]It is hafnium, sulfur, etc. which are contained in strontium which may contain a small amount of impurities in each composing element in this multiple oxide as long as it is not the quantity which bars the above-mentioned operation, for example, is contained in barium, cerium contained in a lanthanum, neodymium, samarium, or a zirconium.

[0028]If quantity from which the operation is obtained contains said multiple oxide powder in a catalyst, although content in particular is not limited, its thing for exhaust gas purification containing catalyst 1L per 30-100g of this invention is preferred from a point of obtaining enough and significant NO_x absorption.

[0029]The catalyst for exhaust gas purification of this invention can acquire a NO_x cleaning effect which is not acquired if respectively independent by making said precious metals and a multiple oxide live together. That is, when exhaust gas atmosphere becomes Lean, high NO_x purification performance is obtained by NO_x absorption by a multiple oxide in a catalyst for exhaust gas purification of this invention. If this multiple oxide carries out NO_x absorption and exhaust gas atmosphere changes from Lean to RICH, NO_x will be emitted from this multiple oxide and high NO_x purification performance will be obtained. NO_x purification performance which was not obtained only by mixing an independent thing of each ingredient which constitutes this multiple oxide, and was excellent is obtained.

[0030]Other catalysts for exhaust gas purification of this invention comprise structure which provided two-layer at least on a fireproof inorganic carrier, and provide a layer which does not contain the above-mentioned multiple oxide in a lower layer for a layer containing the above-mentioned multiple oxide in the upper layer.

[0031]Thus, it will multilayer-structure-size, and NO_x emitted at RICH - the time of rich can be efficiently purified by making a inner layer contain a multiple oxide, and a fall of HC purification function of the three way component catalyst functions can be controlled. Namely, it is good to arrange in the upper layer which does not contain a multiple oxide, in order to purify discharge NO_x effectively, By considering it as such a structure, NO_x will be absorbed by a inner layer containing a multiple oxide, discharge NO_x will be purified in the upper layer which does not contain a multiple oxide, and still more sufficient three way component catalyst function can be obtained.

[0032]As for mean particle diameter (median size) of material which constitutes a catalyst bed of this invention, it is preferred that it is 4 micrometers or less. By making particle diameter into such a range, NO_x absorptance at the time of Lean can be raised.

[0033]That is, NO_x absorption which was excellent when a catalyst for exhaust gas purification made gas flow speed late can be demonstrated, and such an effect is attained by considering it as mean particle diameter of a mentioned range, and, as a result, can acquire high NO_x absorption activity.

[0034]By considering it as this mean particle diameter, the desirable precious metals supported suitably in an exhaust gas catalyst of this invention can be high-decentralized, and NO_x absorption can also be raised.

[0035]As for mean particle diameter, in order to raise said effect further especially, it is preferred that it is 2-4 micrometers. Mean particle diameter in this specification is

measured with a laser diffraction type particle-size-distribution meter.

[0036]After it mixes to composition ratio of a multiple oxide for which it asks and a multiple oxide used for this invention carries out temporary calcination of a nitrate of each composing element of a multiple oxide, acetate, carbonate, citrate, the hydrochloride, etc., it is ground, A nitrate of solid phase reaction which carries out heat treatment calcination, and each composing element of a multiple oxide, acetate, Carbonate, a hydrochloride, citrate, etc. are mixed to composition ratio of a multiple oxide for which it asks, After dissolving in water, can prepare with a coprecipitation method which trickles alkali solutions, such as NH_4OH and NH_3CO_3 , if needed, is made to dry a postprecipitation neutralized precipitate which generated and filtered a sediment, and is calcinated, but. It is not limited to these methods and a multiple oxide should just be formed also by a method except said.

[0037]By this method, at least a part of each ingredient which constitutes a multiple oxide can be composite-sized.

[0038]It is hafnium, sulfur, etc. which are contained in cerium, neodymium and samarium which may contain a small amount of impurities in a raw material for catalyst preparation of a multiple oxide used by this invention as long as it is not the quantity which bars the above-mentioned operation, as described above, for example, are contained in a rare earth metal, and a zirconium.

[0039]Although it can be used combining an inorganic acid salt, carbonate, ammonium salt, organic acid salt, a halogenide, an oxide, sodium salt, an ammine complex compound, etc. as a precious-metals raw material compound of the precious metals used for this invention, It is preferred to use a water-soluble salt especially from a viewpoint of raising catalyst performance. Unless it is not limited to a method special as a method of supporting a porous body of the precious metals but is accompanied by remarkable maldistribution of an ingredient, various methods, such as the publicly known evaporating method, a sedimentation method, the impregnating method, and an ionic exchange method, can be used. A point which improves dispersibility to especially support to alumina to the impregnating method is preferred.

[0040]When based on an ionic exchange method and the impregnating method, since a metallic raw material is used with a solution in many cases, it can add acid or a base in the solution, and can also adjust pH. By adjusting pH, high distribution support may be able to be carried out further.

[0041]A catalyst for exhaust gas purification of this invention can be acquired by it being preferred to support and use for an integral-construction type carrier as for a catalyst of this invention, and grinding a multiple oxide and a precious-metals support inorganic carrier, considering it as a slurry, carrying out a coat to catalyst support, and calcinating at temperature of 400-900 **.

[0042]A grinding method in particular of hitting grinding a multiple oxide and a precious-metals support inorganic carrier cannot be limited, but can carry out the wet milling of the aqueous slurry which contains these preferably, and can use a method of adjusting so that mean particle diameter may be set to 4 micrometers or less.

[0043]A device in particular that can be used for grinding is not limited, but can use a commercial ball type vibration mill, adjusts a ball diameter, grinding time, amplitude, and vibrational frequency, and obtains desired particle diameter.

[0044]A honeycomb carrier, a metal carrier, etc. which have the monolith structure which can use it choosing suitably from publicly known catalyst support as catalyst support for example, which consists of a fireproof material are mentioned.

[0045]Although many things of quality of cordierite, such as ceramics, are used generally [although not restricted / it is preferred to usually use it with honeycomb shape, and] as this honeycomb material, especially shape of this catalyst support, It is also possible to use a honeycomb which consists of metallic materials, such as ferrite series stainless

steel, and also the catalyst powder itself may be fabricated to honeycomb shape. By making shape of a catalyst into honeycomb shape, since a catalyst-surfaces product of a catalyst and exhaust gas becomes large and pressure loss is also suppressed, when using as an object for cars, etc., it is very advantageous.

[0046] Although a catalyst for exhaust gas purification in particular of above-mentioned this invention does not have the service condition limited, an air-fuel ratio can use it for 10-50, and a lean burn engine car by which an air-fuel ratio repeats 10-14.8, and the range of 15-50 still more preferably preferably. By considering it as such directions for use, a cycle of NO_x absorption and discharge is materialized very effectively, and NO_x purification especially with sufficient efficiency of it is attained. Namely, by an air-fuel ratio's absorbing NO_x in a field (lean area) where an air-fuel ratio of 10-50 within the limits is big, and purifying NO_x in a field (rich and/or SUTOIKI) where an air-fuel ratio is small, High NO_x purification performance can be obtained and fields of a still more suitable range where 10 to 14.8 and an air-fuel ratio have a big field where an air-fuel ratio is small are 15-50.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, a following example and comparative example explain this invention. Activated alumina powder was impregnated, example 1 nitric-acid Pd solution was calcinated at 400 ** after desiccation and among the air for 1 hour, and Pd support alumina powder (powder 1) was obtained. Pd concentration of this powder 1 was 2.8 % of the weight. Activated alumina powder was impregnated, dinitrodiamine Pt solution was calcinated at 400 ** after desiccation and among the air for 1 hour, and Pt support alumina powder (powder 2) was obtained. Pd concentration of this powder 2 was 2.8 % of the weight. Activated alumina powder was impregnated, nitric acid Rh solution was calcinated at 400 ** after desiccation and among the air for 1 hour, and Rh support alumina powder (powder 3) was obtained. Rh concentration of this powder 3 was 0.7 % of the weight.

[0048] Citrate was added to lantern carbonate and the mixture of the zirconium nitrate, it calcinated at 700 ** after desiccation, and La-Zr multiple oxide powder (powder 4) was obtained. This powder 4 was lantern/zirconium =5/5 in the metal atom ratio.

[0049] 90 g and the above-mentioned powder 4 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 180 g and the above-mentioned powder 2 was carried out for the above-mentioned powder 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having made this slurry liquid adhere to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (A) of the coated layer weight [of 125 g/L]-carrier was acquired.

[0050] 90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the above-mentioned powder 2 was carried out for the above-mentioned powder 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having made this slurry liquid adhere to the above-mentioned catalyst (A), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 250 g/L]-carrier was acquired.

[0051] The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having replaced La of the example 2 powder 4 with Nd.

[0052] The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having replaced La of the example 3 powder 4 with Pr.

[0053] 180 g and the powder 4 were thrown into 180 g, the water 720g was fed into the magnetic ball mill, preferential grinding of 180 g and the powder 2 was carried out [the powder 1 obtained in example 4 Example 1] for 180 g and the powder 3, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having made this slurry liquid adhere to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification

of the coated layer weight [of 250 g/L]-carrier was acquired.

[0054]The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having used the activated alumina powder which did 6 mol% addition of La instead except for the comparative example 1 powder 4.

[0055]The catalyst for exhaust gas purification was acquired by the same method as Example 1 except having prepared the mean particle diameter of comparative example 2 slurry to 8 micrometers.

[0056]90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in comparative example 3 Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (B) of the coated layer weight [of 125 g/L]-carrier was acquired.

[0057]90 g and the powder 4 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the catalyst (B), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 250 g/L]-carrier was acquired.

[0058]60 g and activated alumina were thrown into 120 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out [the powder 1 obtained in comparative example 4 Example 1] for 90 g and the powder 4, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (C) of the coated layer weight [of 125 g/L]-carrier was acquired.

[0059]90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the catalyst (C), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 250 g/L]-carrier was acquired.

[0060]90 g and the powder 4 were thrown into 360 g, the water 540g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in comparative example 5 Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst (D) of the coated layer weight [of 187.5 g/L]-carrier was acquired.

[0061]90 g and the powder 3 were thrown into 180 g, the water 360g was fed into the magnetic ball mill, preferential grinding of 90 g and the powder 2 was carried out for the powder 1 obtained in Example 1, and slurry liquid was obtained. The mean particle diameter of the slurry at this time was 2.8 micrometers. After having adhered this slurry liquid to the catalyst (D), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the catalyst for exhaust gas purification of the total coated layer weight [of 312.5 g/L]-carrier was acquired.

[0062] In comparative example 6 Example 1, except having used La_2O_3 45g ZrO_2 135g instead of the powder 4, it is the same method as Example 1, and the catalyst for exhaust gas purification was acquired.

[0063] In comparative example 7 Example 1, except that the ratio of La to Zr set the powder 4 to $\text{La/Zr}=1/9$, it is the same method and the catalyst for exhaust gas purification was acquired.

[0064] The catalyst presentation of the catalyst for exhaust gas purification acquired by said Examples 1-4 and the comparative examples 1-7 is shown in Table 1.

[0065]

[Table 1]
組 成 表

	貴金属(g/L)			コ-ト 層 構 造	複 合 酸化物 の位置	複 合 酸化物量 (g)	スラリー 粒 径	複合酸化物組成
	P t	P d	R h					
実施例 1	1.75	1.75	0.43	2 層	下層	180	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
実施例 2	1.75	1.75	0.43	2 層	下層	180	$2.8\mu\text{m}$	$\text{Nd}_{0.5}\text{Zr}_{0.5}\text{O}_x$
実施例 3	1.75	1.75	0.43	2 層	下層	180	$2.8\mu\text{m}$	$\text{Pr}_{0.5}\text{Zr}_{0.5}\text{O}_x$
実施例 4	1.75	1.75	0.43	1 層	—	180	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 1	1.75	1.75	0.43	2 層	下層	180	$2.8\mu\text{m}$	$\text{La}6\text{mol}\%\text{-Al}_2\text{O}_3$
比較例 2	1.75	1.75	0.43	2 層	下層	180	$8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 3	1.75	1.75	0.43	2 層	上層	180	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 4	1.75	1.75	0.43	2 層	下層	60	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 5	1.75	1.75	0.43	2 層	下層	360	$2.8\mu\text{m}$	$\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_x$
比較例 6	1.75	1.75	0.43	2 層	—	La_2O_3 45g ZrO_2 135g	$2.8\mu\text{m}$	$\text{La}_2\text{O}_3+\text{ZrO}_2$
比較例 7	1.75	1.75	0.43	2 層	下層	180	$2.8\mu\text{m}$	$\text{La}_{0.1}\text{Zr}_{0.9}\text{O}_x$

[0066] About the catalyst for exhaust gas purification acquired by the example of examination aforementioned examples 1-4, and the comparative examples 1-7, catalytic activity evaluation after the first stage and durability was performed on condition of the following. The automatic evaluation device using the model gas which imitated the exhaust gas of the car was used for activity evaluation.

[0067] The durable condition engine 4400cc exhaust system was equipped with the catalyst, with the catalyst inlet temperature of 700 **, it operated for 50 hours and durability was performed.

[0068] Evaluation condition catalytic activity evaluation equips the exhaust system of an engine with a displacement of 2000 cc with each catalyst, After that for 60 seconds by $\text{A/F}=14.6$ (SUTOIKI state) $\text{A/F}=22$ (lean atmosphere) For 10 seconds, After that operation for 10 seconds by $\text{A/F}=50$ (lean atmosphere) 1 cycle deed, The average inversion rate was measured respectively, the average inversion rate in this $\text{A/F}=14.6$ (SUTOIKI state), the average inversion rate in $\text{A/F}=22$ (lean atmosphere), and the average inversion rate in $\text{A/F}=50$ (lean atmosphere) were averaged, and it was considered as the total inversion rate. This evaluation was respectively performed after the first stage and durability, and the

following formulas determined the catalytic activity evaluation value. However, catalyst inlet temperature was 350 **.

[0069]

[Equation 4]

$$\text{NOx 転化率(\%)} = \frac{[\text{触媒層入口NOx濃度}] - [\text{触媒層出口NOx濃度}]}{[\text{触媒層入口NOx濃度}]} \times 100$$

(HC, CO も同様)

[0070] The catalytic activity evaluation result obtained as a total inversion rate is shown in Table 2. Compared with the comparative example, catalytic activity of the example was high, and the effect of this invention mentioned later was able to be checked.

[0071]

[Table 2]

評価結果

	転化率 %					
	初期			耐久後		
	HC	CO	NOx	HC	CO	NOx
実施例 1	97	99	90	96	98	80
実施例 2	98	99	88	95	98	76
実施例 3	97	99	89	95	98	78
実施例 4	97	99	89	94	96	73
比較例 1	98	99	82	96	98	60
比較例 2	98	99	85	96	98	70
比較例 3	97	99	89	92	96	60
比較例 4	97	99	89	96	96	69
比較例 5	97	99	90	96	98	82
比較例 6	98	99	82	96	98	59
比較例 7	98	99	80	96	98	50

[Translation done.]